1 Introduction

3D printing or additive manufacturing (AM) is described as the process of making a three-dimensional solid object from a digital file using additive processes. A 3D object is created by depositing successive layers of a material according to a computer design.

To print a 3D object, first one needs to have the design. A completely new object can be made in CAD (computer-aided design) file using a 3D-modeling program, such as SolidWorks® or AutoCad®. Alternatively, the copy of an existing object can be made by scanning it using a 3D scanner. Using appropriate software, the 3D model is sliced into horizontal layers, and loaded onto a 3D printer. The 3D printer builds the final object one layer at a time.

A large number of 3D printing techniques is now available, the main differences between them being the way layers are deposited and the materials used. Amongst them, laser-based techniques are very popular, as the laser beam can be focused and directed very accurately.

In this chapter we will detail and compare the most popular laser-based 3D printing techniques. In Sections 2 and 3 and we will describe Stereolithography (SLA) and Selective Laser Sintering (SLS), the most industrial of the laser-based 3D printing techniques. In Section 4 we will concentrate on microscale 3D printing techniques: projection stereolithography (PSL, Section 4.1) and multiphoton lithography (MPL, Section 4.2); We will describe extensively the principles and applications of the latter, the most popular and widely used of all microscale 3D printing techniques. Finally, in Section 5, we will describe how lasers are used to structure the surface of polymers, glasses, semiconductors, and metals.

2 SLA

SLA is an AM technology for producing 3D objects in a layer-by-layer fashion, by photopolymerizing a photosensitive material with an ultraviolet (UV) laser. The father of SLA is Charles (Chuck) W. Hull; he first coined the term ‘stereolithography’ and described the apparatus in the 1986 patent “Apparatus for production of three-dimensional objects by stereolithography.” There, it is described as "a new and improved system for generating a three-dimensional object by forming successive, adjacent, cross-sectional laminae of that object at the surface of a fluid medium capable of altering its physical state in response to appropriate
synergistic stimulation, the successive laminae being automatically integrated as they are formed to define the desired three-dimensional object. It is basically describing a system for making solid objects by successively curing thin layers of a photo-polymer using UV light. The patent described a focused UV light beam drawing each layer of the object onto the surface of a vat filled with liquid resin, as shown in Figure 1. Also in 1986, C.W. Hull founded 3D Systems Inc., the first company to develop a commercial SLA system.

In a commercial SLA machine, a focused UV laser beam – nowadays usually the 3rd harmonic of an yttrium aluminum garnet (YAG) laser – is used to photopolymerize an acrylate or epoxy liquid resin. The first (usually sacrificial) layer of the component is built on an elevator platform. At every layer and always according to a CAD design, the beam draws a pattern on the surface of the liquid resin, selectively solidifying it and making it adhere to the layer below. After each layer has been 'written,' the elevator platform lowers by a single layer, the built section is re-coated with liquid resin (made flat by employing a re-coating blade), and another layer is 'written.' After the completion of the laser writing, the unexposed photopolymer is removed by immersing the structure in a solvent that dissolves the liquid monomer, and not the polymerized material. To save time, each layer is not fully photopolymerized, but instead the laser traces its exterior, and crosshatches in between. This results in a slice with a honeycomb interior and solid skins on top and bottom, encapsulating liquid resin. After removing the unexposed resin, the 3D object is 'baked' in a UV 'oven,' to solidify the encapsulated liquid resin. Very often the objects made by SLA need to have supporting structures, to avoid deformation due to the piston movement, gravity, and the re-coating blade. These supports need to be removed manually after the completion of the building process.

SLA can produce almost infinitely complex functional prototypes in a time length from a few hours to more than a day. The resolution can be down to 5 μm, while the overall size depends on the type of the machine and the size of the elevator platform. Typically, an SLA machine will be capable of producing components of maximum size 50 × 50 × 60 cm³. However, nowadays there are SLA machines, such as the Mammoth, that can produce sizes up to 2 m. On the downside, both photosensitive resins and SLA machines can be very expensive.

The main application of SLA is prototyping: as such, it has been employed by a variety of industries, from medical prototyping to the car industry, where it is routinely used to make polymer prototypes of car engines.

However, the use of SLA models is not limited to prototypes; modern SLA resins provide strong enough models to be machined and make functional synthetic parts, but they are mostly used as master patterns for injection molding and metal casting.

SLA has also been applied in medicine, to fabricate guides for tumor identification and surgery guidance, but also for the fabrication of implants and scaffolds for bone and cartilage tissue engineering. The materials used in this case can be pure photopolymers, or custom materials such as resins mixed with hydroxyapatite.

3 SLS

The SLS technique employs a high-power laser to sinter layers of material in powder form, in order to build 3D structures. A typical experimental setup is shown in Figure 2. A layer of powder is first deposited on a fabrication piston substrate. The laser beam is scanned over the powder surface following a CAD design. The laser beam heats the powder to melting point and causes the powder particles to melt together to form a solid mass. Subsequent layers are built directly on top of the earlier layers, with new layers of powder deposited on the top of the already sintered layers using a roller.

The materials used for building components in SLS machines can be single component powders (such as metal powders produced by ball milling) or, more commonly two-component powders, coated powders or powder mixtures. Compared to other
3D laser printing techniques, SLS can build components from a wide variety of materials. These can be polymers such as nylon and nylon-coated metal particles, polystyrene, metals such as titanium, steel, alloys, and several biomaterials such as hydroxyapatite, polycaprolactone, polylactide, and mixtures of those with other biopolymers. Depending on the material, up to 100% density can be achieved with material properties comparable to those from conventional milling methods.

Due to its material versatility and its potential to make very complex geometries directly from computer models, SLS is widely used nowadays. While its original use was in prototyping, it is now used also in custom or limited-run manufacturing to produce end-use parts. One such area is dental implants and scaffolds for hard and soft tissue engineering. SLS has been extensively used to create hard scaffolds for bone and cartilage tissue engineering, often employing mixtures of polycaprolactone with calcium phosphates as a scaffold material. In soft tissue engineering its use has been more limited; it

![Figure 2](http://www.britannica.com/technology/3D-printing/images-videos — Encyclopedia Britannica).

![Figure 3](a) A dental implant made using SLS and (b) poly-ε-caprolactone scaffolds made using SLS for cardiac regeneration.
has been used to melt together poly-e-caprolactone layers for cardiac regeneration\textsuperscript{81,82}, biodegradable polycaprolactone was also structured in order to grow avidin–biotin human hepatoma Hep G2 cells, for liver tissue engineering. SLS has also been used to make replication masters for biomedical implants.\textsuperscript{83}

4 Microscale 3D Printing Techniques

Progress in technologies such as MEMS and microfluidics has increased the requirement for 3D printing technologies with micro and nano features resolution, using diverse materials, such as ceramics and polymers. In the following paragraphs we describe two laser-based 3D microfabrication techniques: Projection micro-stereolithography and multiphoton lithography.

4.1 Projection Micro-Stereolithography

In Section 2 we described SLA as a technique for fabricating large-scale components and prototypes. The same technique was miniaturized to produce micron scale components,\textsuperscript{84} and is now called micro-stereolithography (\textmu SLA). The procedure is exactly the same as in classic SLA, except the beam is focused very tightly, to enable high resolution.

While \textmu SLA worked well, it never became popular for mass production as it was very slow. To overcome this problem, Alain Bertsch and co-workers proposed a new system based on a dynamic mask pattern being projected on the liquid resin surface, therefore photopolymerizing each layer of the pattern in one shot.\textsuperscript{85,86} The experimental setup is shown in Figure 4. There, the beam of a green laser (515 nm) was modulated by a liquid crystal display (LCD), to project an image on a platform immersed into the photosensitive resin. As each component layer is made using a single light exposure, the only moving part in the system is the \textit{z}-axis of the component platform.

As the Bertsch system was designed to operate with green light (a wavelength of transparency of the LCD display), it could not use any of the commercially available photosensitive resins designed for classic SLA. This was accomplished by the Chatwin group (Sussex University, UK), who replaced the LCD with a custom-made spatial light modulator (SLM), transparent to the UV.\textsuperscript{87–89} Several materials composed for SLA and high-resolution structures were made using this technique (Figure 5).\textsuperscript{87–90}

![Figure 4](image)

**Figure 4** The first projection \textmu SLA set-up using an liquid crystal display as a dynamic mask.\textsuperscript{85,86}

![Figure 5](image)

**Figure 5** 3D structures fabricated using an spatial light modulator as a dynamic mask.\textsuperscript{89}
Replacing LCDs with SLMs solved the material availability problem but generated others: the low switching speed and low optical density of the refractive elements of the SLM during the OFF mode reduce the contrast of the transmitted pattern. In addition, the SLM UV transparency is limited, resulting in energy wastage and overheating (therefore limited lifetime) of the device itself.

At the same time as the Chatwin team developed SLM-based µSLA, digital micromirror devices (DMDs) became available by Texas Instruments. DMD is a reflective array of fast, digital light switches that are monolithically integrated onto a silicon address chip. Used as a projection system, a DMD replaced the SLM in a system implemented by Sun et al., providing high-quality, seamless, all-digital images with exceptional stability and minimal power loss. The quality and resolution of the structures fabricated using this technique was superior to anything presented before (Figure 6).

The application of DMDs in µSLA is still fairly limited, and most research has focused on improving the process rather than developing applications. Again, however, the main area of research applications has been developing microenvironments for cell growth.

4.2 Multiphoton Lithography

Multiphoton Lithography based on the Multiphoton Polymerization of photosensitive materials is a direct laser writing technique that allows the fabrication of three-dimensional structures with submicron resolution. The polymerization is based on two-photon absorption (TPA); when the beam of an ultrafast laser is tightly focused into the volume of a transparent, photosensitive material, the polymerization process can be initiated by nonlinear absorption within the focal volume. By moving the laser focus three-dimensionally through the material, 3D structures can be fabricated. The technique has been implemented with a variety of acrylate and epoxy materials and several components and devices have been fabricated such as photonic crystal templates, mechanical devices, and microscopic models. Resolution below 100 nm has been achieved using this technique.

The unique capability of MPL lies in that it allows the fabrication of computer-designed fully 3D structures with resolution beyond the diffraction limit. No other competing technology offers these advantages. Classic 3D prototyping techniques such as UV laser SLA, 3D inkjet printing, and laser sintering can also produce fully three-dimensional structures; however, they cannot provide resolution better than a few microns. On the other hand, lithographic techniques with superior resolution, such as e-beam lithography, cannot produce anything more complicated than high-aspect ratio two-dimensional structures.

In this section we summarize the principles of microfabrication by MPL. We discuss the fundamental principles of multiphoton absorption (MPA) and describe a typical MPL experimental setup. Then we concentrate on materials used for MPL microfabrication, on recent progress in the functionalization of the surface and the bulk of the 3D-fabricated structures, while at the same time discussing applications of the technology.
4.2.1 Multiphoton polymerization

The basis of MPL is the phenomenon of MPA. For simplicity, we will discuss TPA and two-photon polymerization (TPP)—the same rules apply to more than two photons.

There are two types of TPA: sequential and simultaneous. In sequential, the absorbing species is excited to a real intermediate state, then, a second photon is absorbed. The presence of the intermediate energy state implies that the material absorbs at this specific wavelength; it will therefore be a surface effect and will follow the Beer–Lambert law. The simultaneous absorption, on which the MPL technique is based, was originally predicted by Maria Göppert-Mayer in 1931 in her doctoral dissertation. It is defined as "an absorption event caused by the collective action of two or more photons, all of which must be present simultaneously to impart enough energy to drive a transition." This prediction was not experimentally verified until over 30 years later by Werner Kaiser, when the invention of the laser permitted the first experimental verification of the TPA through the two-photon excited fluorescence detection in a europium-doped crystal. In simultaneous absorption, there is no real intermediate energy state, i.e., the material is transparent at that wavelength. Instead, there is a virtual intermediate energy state and TPA happens only if another photon arrives within the virtual state lifetime. For this to occur high intensities are required, which can only be provided by a tightly focused femtosecond (fs) laser beam. This is illustrated in Figure 7; as it can be seen, the electron transition in this case is caused by two photons of energy $hv/2$ rather than one of energy $hv$.

Ti:Sapphire and near-infrared lasers are widely used for this purpose. They have two main advantages: firstly they have very short pulses, in the order of a few tens of femtoseconds, so they do not cause thermal damage. Secondly, their standard wavelength is 780–820 nm, which is twice the wavelength of polymerization of a wide range of photopolymers. In addition, most photo-polymers are transparent at around 800 nm, which allows in-volume focusing of the laser beam with minimal scattering.

When the laser is focused tightly into the material, the photoinitiator used to initiate the polymerization will absorb two or more photons and produce radicals. As the material response is proportional to the square of the intensity, this will only happen at the focal point, which, combined with the fact that the two-photon transition rate is very small, will provide very high-spatial resolution.

Photopolymerization is a light-induced reaction, which converts a liquid or gel monomer into a solid polymer. These reactions require the use of an appropriate photoinitiator, which is a light sensitive molecule that produces an active species upon irradiation with UV, visible, or infrared light. The photoinitiators that have been most extensively used so far are divided into two main categories depending on the nature of generated active species (radicals or cations). An effective initiator has a high-quantum yield in the generation of the active moieties, high-thermal stability and stability in darkness, and is highly soluble in the polymerization medium.

Free-radical polymerizations are chain reactions in which the addition of a monomer molecule to an active chain-end regenerates the active site at the chain-end.

The free-radical photopolymerization mechanism involves at least three different kinds of reactions (Eqn [1a]–[1b]):113–115

- The first step is the initiation during which the free-radical initiator is decomposed with light in the presence of monomer to form an active species (Step 1a).
- In the next step, known as the propagation, the initiator fragment reacts with a monomer molecule to form the first active adduct that is capable of being polymerized. Monomers continue to add in the same manner resulting in the formation of macroradicals which are end-active polymers (Step 1b).
The final step is the termination during which the growth center is deactivated and the final polymer molecules are formed. This step normally involves the reaction between two polymers bearing active centers and can proceed by two different mechanisms, combination or disproportionation, leading to the formation of one or two polymers chains, respectively (Step 1c).

Equations [1a]–[1b] show the TPP process

\[
\begin{align*}
\text{Initiation} & : I \xrightarrow{h \nu, h \nu} I^* \rightarrow R^* \quad [1a] \\
\text{Propagation} & : R^* + M \rightarrow RM^* \xrightarrow{M} RM\cdots \rightarrow RM_n^* \quad [1b] \\
\text{Termination} & : RM_n^* + RM_m^* \rightarrow RM_{n+m} R \quad [1c]
\end{align*}
\]

Besides the above, other reactions, such as chain transfer and chain inhibition, often take place and complicate the mechanism of free-radical polymerization.

Photopolymerizations follow the general scheme for any polymerization, however, the use of light, rather than heat, to drive the reaction has certain advantages, such as the elimination of solvent, the high-reaction rates at room temperature, and the spatial control of the polymerization.

### 4.2.2 The diffraction limit

Theoretically, the highest resolution that can be achieved by a focused laser beam is given by Abbe’s diffraction limit (eqn [2]).

\[
\text{Diffraction limit} = \frac{0.5 \lambda}{\text{N.A.}}.
\]

where $\lambda$ is the laser wavelength and N.A. is the numerical aperture of the focusing objective; this has fueled the race for ever decreasing wavelengths, such as electron wavelengths and for alternative, non-light patterning techniques such as atomic force microscopy and near-field scanning optical microscopy, however, these techniques only allow surface and not in-volume patterning. To produce 3D structures with in-volume patterning, and produce photopolymerized voxels smaller than that defined by the diffraction limit, materials with well-defined photopolymerization threshold need to be used.

As the photoinitiator is excited by the laser process, it produces radicals; these radicals are quenched by oxygen and other quenchers in the system. Quenching is a competing effect to photopolymerization and is usually considered detrimental to the process. In MPL, however, it can be used to circumvent the diffraction limit and produce structures of very high resolution. This can be done by modifying the light intensity at the focal volume, in a manner so that the light-produced radicals exceed the quenchers and initiate polymerization only at a region where exposure energy is larger than the threshold. In this case the diffraction limit becomes just a measure of the focal spot size and it does not really determine the voxel size.

### 4.2.3 Experimental set-up

A typical experimental setup for the fabrication of three-dimensional microstructures by MPL is shown in Figure 8. The laser source typically is a Ti:Sapphire femtosecond oscillator operating at 800 nm; there are also examples in literature where an Optical Parametric Oscillator is used with a Ti:Sapphire laser, to reduce the laser wavelength to visible wavelengths. The laser will typically have a pulse length of less than 200 fs and a repetition rate of 50–80 MHz. The energy required for the polymerization process will depend on the material, the photoinitiator and the focusing, but is usually in the order of a few nanojoules per pulse.

The photopolymerized structure is usually generated in a layer-by-layer format. Each layer is formed either using an $x$–$y$ galvanometric mirror scanner or $x$–$y$ piezoelectric stages. The main difference between the two cases being that in the former case, the structure remains immobile and the structure is generated by the laser beam moving, while in the latter case the $x$–$y$ stages move the structure and the laser beam remains immobile. Movement on the $z$-axis can be achieved using a piezoelectric or a high resolution linear stage.

To achieve the tight focusing conditions required for TPP to occur, a microscope objective needs to be used; when the numerical aperture of the objective is higher than 1, immersion oil is used for index matching. Galvo scanners have to be adapted to accommodate microscope objectives, as usually they are designed to take lenses with long focal lengths.

Beam control can be achieved by either using a fast mechanical shutter or an acousto-optic modulator, while beam intensity control can be achieved using neutral-density filters, a variable attenuator, or a combination of a polarizer and a waveplate.

For the online monitoring of the photopolymerization process a charge-coupled device camera can be mounted behind a dichroic mirror, as shown in Figure 8. This is possible as the refractive index of most photopolymers changes during polymerization, so that the illuminated structures become visible during the building process.

When the photosensitive polymer is in a liquid form, in order to avoid liquid movement as the samples moves, the samples are prepared in a sandwich format between two thin glass coverslips; a spacer needs to be used to maintain sample uniformity. When the sample is a solid or a gel, then there is no need for the sandwich format. To avoid the distortion of the focused laser beam by the built structures, they are fabricated layer-by-layer bottom up with the last layer attached to the glass coverslip.
After the completion of the photopolymerization process and in order to remove the unphotopolymerized resin, the samples need to be developed like in any lithographic process. The developer used and the time for development will depend on the material.

The experimental procedure for fabricating a 3D structure by MPL is shown in Figure 9: (1) The laser beam is tightly focused into the volume of the material. (2) Either the focused beam or the sample move following a computer-generated pattern. (3) After the laser writing of the structure, the sample is immersed into an appropriate developer. (4) The freestanding structure is revealed.

![Figure 8](image8.png) A typical setup for multiphoton polymerization, consisting of a fs laser, a galvanometric mirror scanner, moving stages, directional and focusing optics, and a monitoring camera.

![Figure 9](image9.png) MPL experimental procedure (I) beam focusing, (II) laser writing, (III) development, and (IV) completed structure.

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### 4.3 Materials for Laser Polymerization

#### 4.3.1 Introduction

In general, a material suitable for structuring with MPL includes at least two components: (1) a monomer, or a mixture of monomers/oligomers, which will provide the final polymer and (2) a photoinitiator, which will absorb the laser light and provide the active species that will cause this polymerization. Several monomer/oligomer and photoinitiator combinations have been used for this purpose. These are mostly negative photoresists such as hydrogels, acrylate materials,\(^1\) the epoxy-based photoresist
SU-8,102 and hybrid materials.103,128 Recently, redox and Diels–Alder photopolymerization have been also been reported.129,130 In the following sections, we will discuss briefly these photoinitiators and materials.

4.3.2 Photoinitiators

During polymerization, a monomer is converted into polymer and this transformation can be induced by light. In classic photolithography, a photoinitiator absorbs the light and produces an active species which causes the photopolymerization. In TPP, however, things are more complicated, and these extra requirements must be fulfilled:101,126

- Both the photoinitiator and the monomer/oligomer are transparent at the laser wavelength used, so that the laser beam can be focused inside the volume of the material without being absorbed at the surface.
- The monomer/oligomer needs to be transparent at the TPA wavelength (\(\lambda/2\)); if it is not, then the photopolymer is likely to be burnt or ablated.
- The photoinitiator needs not only to absorb at the two-photon wavelength, but also to have a high two-photon cross-section, a high radical quantum yield and highly-active radical species generated; typically, if any two of these three are large enough, the initiator will normally be efficient for TPP.

In classic lithography, there are two types of photoinitiators: radical photoinitiators and cationic photoinitiators. All the materials developed to date for MPL employ radical photoinitiators; these, upon light irradiation, generate free radicals, which initiate a polymerization process of acrylates or vinyl ethers. Cationic initiators are photo-acid generators that produce cations upon light irradiation and are used for the polymerization of epoxides or vinyl ethers;113–115 to the best of our knowledge, there are no materials to date, specifically developed for MPL employing cationic polymerization, however, it is employed in the most commonly used photolithography resist, SU-8.

An effective MPL photoinitiator has a high quantum yield in the generation of the active moieties, high thermal stability and stability in darkness, and is highly soluble in the polymerization medium.131 The most commonly used free-radical photoinitiator is benzophenone and its derivatives.132,133

Nowadays, there is a lot of concentrated effort to synthesize fast and efficient photoinitiators specifically for multiphoton applications.134 In addition, there is a lot of work toward biocompatible photoinitiators, specifically for bio-applications. To this end, classic dyes such as Bengal Rose, Eosin, Nile Red, biomolecules such as flavin mononucleotide, but also novel, synthetic photoinitiators have been used.127,131,135–141

4.3.3 Organic photopolymers

The first materials used for MPL were acrylate photopolymers142 (Figure 10). These materials have several properties which make them attractive for MPL applications: a wide variety of the full composites or their monomers are commercially available; they are transparent at visible and near-infrared wavelengths, and can therefore be processed by IR and green ultrafast lasers; they can be developed in common, nonaggressive solvents such as isopropanol; they can be polymerized fast and with low shrinkage and, after polymerization, they are mechanically and chemically stable.

Due to their versatile chemistry, acrylate photopolymers have been used in their pure form but also doped with other materials to add them functionality. They have been doped with TiO2 nanoparticles to increase their refractive index for photonic crystal applications;41 with CdS nanoparticles for the fabrication of light-emitting 3D structures (Figure 11);144,145 with metal-binding materials to cover them with metals using electroless plating;136,137 with chitosan to make them suitable for bio-applications;140 with Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) to make them electroluminescent.149

![Figure 10](https://example.com/figure10.png)

Figure 10  The first 3D structure fabricated by MPL.142
4.3.3.1 SU-8

SU-8 is a negative, epoxy-based photo-resist commonly used for the fabrication of high-aspect ratio structures, using standard contact lithography. Its absorption maximum is at 365 nm. When exposed to the appropriate light, SU-8’s long molecular chains cross-link, causing the material to become insoluble to most common solvents. For this to happen, the SU-8 films require postexposure heat treatment.

The possibility to structure SU-8 by MPL polymerization was first demonstrated by Witzgall et al., who employed single shots from Ti:Sapphire femtosecond amplifier to fabricate small dots. More complex 2D and 3D structures were built by Belfield et al. and Kuebler et al., respectively, who worked on the development of novel, efficient photoinitiators for cationic polymerization. Since then, SU-8 has been used by a large of the research teams involved in MPL fabrication have used SU-8.

SU-8 is thermally stable, transparent in the visible and highly resistant to solvents, acids, and bases. These properties make it suitable for permanent use application; by itself, SU-8 has been employed for the fabrication of photonic, microfluidic, and biomedical structures, while it has also been covered with metal for metamaterial fabrication.

4.3.3.2 Hybrid materials

Over the last few years, MPL materials research has focused on the development of photosensitive hybrid composites. Especially silicate-only based photopolymers have proved to be a very popular choice, as they can be commercially available and they combine properties of silicate glasses such as hardness, chemical and thermal stability, and optical transparency with the laser processing at low temperatures of organic polymers; properties impossible to achieve with just inorganic or polymeric materials. The most widely used and studied silicate material is the photopolymer ORMOCER®, commercially available from Microresist Technologies, Germany, and it has been used for a variety of mostly photonic applications, like the optically active polymer microdisk of Figure 13.
ORMOCER® and other silicate-only based hybrid materials have provided the possibility to fabricate high-resolution 3D structures. They do not allow, however, the optimization and ‘fine-tuning’ of the materials properties for specific applications. The versatile chemistry of hybrid composites allows the copolymerization of more than one metal alkoxides; this has been shown to enhance the material’s mechanical stability and allows the modification of its optical properties. There are a few examples of composite photosensitive hybrid materials used in MPL applications;103,133,179,180 Ovsianikov et al. showed that under specific fluence conditions, specific material combinations can be structured into complex 3D structures without shrinkage.181,182 In addition to metal alkoxides, hybrid materials chemistry provides the possibility of the inclusion of functional groups, such as nonlinear optical molecules,183,184 quantum dots,185 and metal-binding materials.186 Zirconium silicates doped with a monomer containing amine moieties were used for the fabrication, for the first time using MPL, of 3D structures selectively metalized with silver (Figure 14).187,188

4.4 Applications

4.4.1 Metamaterials

Metamaterials are artificial materials with properties that do not exist in nature; these properties are due to structure and not material composition. Their name derives from the greek word ‘meta,’ which means beyond, because these materials have properties that extend beyond materials found naturally. In metamaterials, an assembly of structures can replace the role that atoms and molecules have in conventional materials, resulting in a composite structure with electromagnetic properties beyond anything that can be found naturally, or chemically synthesized. An excellent tutorial on metamaterials can be found in the website of Prof. David R. Smith (Duke University).189

Photonic metamaterials consist of nanostructured metalo-dielectric subwavelength building components, and allow the realization of many new and unusual optical properties, such as negative refractive index, magnetism at optical frequencies, perfect absorption, and enhanced optical nonlinearities. Several applications of metamaterials have been proposed, including ultrahigh-resolution imaging systems, compact polarization optics, and cloaking devices.190 The realization of these applications requires the fabrication of large-scale metallo-dielectric structures, a very challenging task. There has been some limited research into the direct
fabrication of metallic 3D structures using multiphoton reduction of metal ions. The quality of the structures, however, has been compromised by the reduced transparency of the metal ion solutions at the laser wavelengths used (500–800 nm).\textsuperscript{191,192} Metallic woodpile structures have also been realized experimentally at micron wavelengths using traditional lithographic techniques.\textsuperscript{193–195} However, lithographic techniques can accommodate only a very limited number of layers, and aligning each layer with the previous one is difficult.

MPL is the only inherently 3D fabrication technique, with the potential to fabricate 3D structures, but the majority of the materials structurable by MPL are dielectrics. A popular approach is to use MPL to make dielectric structures, and subsequently metallize them. The most successful approaches and their advantages and disadvantages are listed in below:

1. MPL of positive photoresists and filling with gold using electroplating.\textsuperscript{196,197} Here, voids are created in a positive tone photoresist using MPL; these are subsequently filled with gold using classic electroplating (Figure 15). The main advantage of this technique is that there is no need to remove the photoresist as the refractive index contrast between the gold and the dielectric material is very high. The main disadvantage is that the number of designs that can be structured is limited, as the right apertures of the material removal and gold filling have to be allowed; therefore, this is fundamentally a 2.5D structuring technique.

2. MPL of dielectric structures and nonselective metallization with electroless plating. Here, a standard photolithographic material is used, such as SU-8, for the fabrication of the structures, and subsequently their surface is covered with silver using classic electroless plating.\textsuperscript{196–201} Additional processing, to enable the metal adhesion on the surface, is required and the quality, structural integrity, and resolution of the structures depend on the building material and the surface-processing step. The advantage of this technique is that any photopolymer can be used; the disadvantages are that, as the density of the metal-binding sites on the structure cannot be controlled, the metallization quality can vary. In addition, along with the surface of the structures, the substrate is also activated; the metallization is therefore not selective, often requiring an extra step to remove the structures from the metalized substrate.\textsuperscript{199}

3. MPL of dielectric structures and selective metallization with electroless plating. Here, a composite doped with the metal-binding sites is employed for the structure fabrication.\textsuperscript{147,186,187} The main advantages in this case are that the metallization is selective, and the density and distribution of the metal-binding sites can be controlled. The main disadvantages are that specific metal-binding materials need to be used, and in most cases these were not able to provide the required resolution and structural integrity required for optical metamaterials. Only very recently it was shown that it is possible to use this method for the fabrication of optical nanophotonic devices.\textsuperscript{187}

4. MPL of dielectric structures and metallization with chemical vapor deposition (CVD). Here MPL is used to fabricate 3D structures by any material, typically SU-8.\textsuperscript{202} The surface of the structures is subsequently activated using plasma etch. Finally, they are covered with silver using CVD. The main advantage of this technique is that any photopolymer can be used, and the resolution and final quality of the structures will depend on that. The main disadvantages are firstly, CVD can only penetrate a small number of structure layers, allowing only a small number of unit cells, and secondly, there is no selectivity; as with the plasma etch, the substrate is activated as well as the structure.

It should also be noted that, recently, there has been reported some work concerning structuring by MPL of transparent conducting materials, such as ionogels.\textsuperscript{203,204} However, neither the conductivity nor the resolution of these materials are sufficient for applications in optical metamaterials.
4.4.2 Biomedical applications

The biomedical applications of MPL can be broadly divided into two categories: biomedical microdevices and scaffolds for cell culture.

The first category, biomedical microdevices, includes devices such as micro Needles for drug delivery, and micromechanic, microfluidic, or optofluidic functional devices.\textsuperscript{205,206} Despite the enormous potential of 3D nanostructuring in this field, there are only few examples to date, mostly because there has not been much research into the integration of MPL-made structure into existing micromechanical systems. Only recently, Amato \textit{et al}. employed MPL to build a cell sorter inside a commercial microfluidic chip.\textsuperscript{207,208} Most other structures reported are freestanding and have not been integrated into a functional device.\textsuperscript{209–216} Special mention should be made to some recent research introducing magnetic materials into the photopolymerizable resin, making possible the contact-free controlled movement to the fabricated devices.\textsuperscript{217,218}

The second category, MPL scaffolds for cell culture studies and tissue engineering, has seen an enormous growth over the last few years (Figures 16 and 17). Tissue engineering is the discipline applying the principles of engineering and life sciences toward the development of biological substitutes that restore, maintain, or improve tissue function or a whole organ.\textsuperscript{219} An important part of the development of artificial tissue is the choice of scaffold, as it can influence the attachment, migration, and proliferation of cells. 3D cell cultures offer a realistic environment where the functional properties of cells can be observed and manipulated.\textsuperscript{220–222} Although producing scaffolds using laser-based, user controlled manufacturing techniques such as MPL or classic SLA is time consuming and therefore costly, recent studies have shown that they can provide tissue engineering solutions for aligned and complex tissue growth. An important advantage is that a controlled topological environment for cell growth can be achieved (Figure 18). In addition, ordered 3D scaffolds are ideally suited for exploring the relationship between 3D topology and cell proliferation. The possibility to manipulate particles in an aqueous solution in order to produce composite material scaffolds with different biological properties selectively localized in space is another advantage of MPL.\textsuperscript{223}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{SEM pictures of a 3D artificial scaffolds. (a) A cubic porous scaffold consisting of horizontal and vertical ring structures in 170-fold magnification and (b) a scaffold cell unit in 550-fold magnification.\textsuperscript{226}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{A freestanding micro-scaffold.\textsuperscript{227}}
\end{figure}
Recent reviews by Raimondi et al., Ovsianikov et al., and Selimis et al. describe in great detail the use of lasers in tissue engineering applications. In this field, most groups have used permanent scaffolds for hard tissue engineering or investigating cell (including stem cell) growth. More recently, there has been a lot of active research into the synthesis of new, biocompatible and biodegradable materials.

5 Laser-Based Surface Texturing Techniques

In general, the assortment of the laser materials processing comprises cutting, drilling, welding, surface hardening, alloying, cladding, rapid prototyping, laser-assisted forming, ablation, and shot peening. In our days, the available laser units can deliver beam with wavelength ranging from the UV to the infrared (IR) spectral region owning continuous or pulsed power density – the laser power may extend from low values (~mW) to extremely high ones as 1–100 W – exhibiting not only both spatial and temporal coherence but low divergence as well. Upon the laser materials processing, a portion of an either pulsed or continuous wave laser beam – which incidents on the material surface – is absorbed, while the greater one is reflected. The absorbed photon energy may lead to excitation of valence and/or conduction band electrons, excited electron–phonon interaction within $10^{-11}–10^{-12}$ s, electron–electron or electron–plasma interaction and electron–hole recombination in a $10^{-9}–10^{-10}$ s timescale. That is to say, extreme heating and cooling rates (typically $10^3–10^{18}$ K s$^{-1}$) are achieved within the laser-treated region and, most importantly, besides the high total deposited energy density ($10^3–10^4$ J cm$^{-2}$), the bulk material temperature is not significantly affected, allowing, thus, the high controlled and precise processing of the material. In any case, toward the achievement of the desired and effective degree of heating and phase transition for the laser surface-processing gamut, the amount of the deposited laser energy density as well as the laser pulse duration should accordingly be picked out. The laser surface processing can be accomplished, grosso modo, either without melting (hardening, bending) requiring low power density, with melting (cladding, welding, cutting) necessitating high power density, or, with vaporization (cutting, drilling, ablation) calling for significantly high power density being deposited at ultrashort pulse duration.

In the present section, we shall focus on techniques aiming to the surface roughness modification relying indicatively on laser ablation and laser texturing. The tailoring of surface roughness and topography is very promising for a plethora of applications and the various results found at the literature for metals, ceramics, glasses, and polymers are presented. In general, the formation mechanism(s) underlying the laser-induced topographies remain under study because of the laser machining (LM) process complexity. They are interpreted in terms of material laser ablation (Figure 19) based on physical models of molecular dynamic simulations, but they do not account for the poorly understood laser-generated effects of plasma plume formation and expansion, oxide formation, optical property changes, nanoparticle shielding, incubation, self-organization as well as for the medium in which the laser processing takes place.

Recently, a detailed theoretical approach concerning the development of various types of self-assembled morphologies, ranging from nano-ripples to periodic microgrooves and quasi-periodic micro-spikes has been reported. For more than 20 years, laser surface texturing (LST) has proven an efficient and controllable method for producing the texture of micropores on magnetic disk drives and ceramics. LST is, nowadays, an efficient and clean to the environment technique which enables the precise shape and dimension control of induced micro-patterns. It is considered to be the most precocious technique for polymer, metal, ceramic, glass, and semiconductor surface engineering toward the control of wettability.
color marking for counterfeit protection, the control and improvement of wear resistance and friction coefficient in tribological contact, biomimetic, and microfluidics purposes. LST, relying on material ablation, induces a regular array of a great number of micro-dimples on a surface which meets many challenges in various lubricated applications by friction reduction in conformal lubricated contacts. Indeed, these dimples serve either as traps for wear debris, as reservoir for lubricant under starved lubrication, or, they may enhance the hydrodynamic lubrication mechanism. There have been performed many theoretical and experimental studies concerning the LST contribution to increase the surface adhesion for bonding and to the tribological performance of: (1) lubricating sliding contacts pinpointing at first place the fluid film lubrication e.g., oil, water, aqueous bovine serum albumin solution but, the solid film lubrication and, the dry one as well, (2) reciprocating automotive components, and (3) diamond-like carbon coatings. The UV lasers, offering the advantage of reduced surrounding surface overheating over the IR ones, they have been adopted in the surface topography modification of ceramic and hard coatings. In advance, LST has also been applied in the fiber laser microgrooves and microholes fabrication on the surface of polycrystalline diamond tools, in the tribological properties improvement of Al2O3/Mo laminated composites at room and high temperatures, of gray cast iron, of titanium alloy combined with diamond-like carbon films coating technology and of hard TiAlSiN coatings combined with high-energy ion implantation.

Besides the many advantages that LST offers, such as noncontact, good flexibility, and high spatial resolution, its broader application is hindered due to the residual stress and the shrinkage cavity generated by thermal effects during LST process. A surface treatment process for improving several mechanical properties, for example, fatigue, durability, corrosion resistance, and wear performance, of metals is the laser shock peening (LSP) one. It is a cold machining process which relies on the laser-generated shock waves able to induce severe plastic deformation of materials surface: a section of the material to be peened is paint coated and a thin film of water runs over the surface, while, a laser beam passes through the water layer being focused onto a particular target location causing the paint layer to vaporize into plasma. Upon plasma expansion, high pressure (GPa-TPa), short duration (ns), shock waves propagate into the water layer, which confines the energy and increases the pressure pulse intensity within the base material under texturing.

It is the amplitude of the laser-induced shock waves that causes the plastic deformation at the surface. LSP has been proposed for the fabrication of micro-dimple arrays on copper surface and, it can be applied as a post-processing method for the improvement of surface layers mechanical properties since it induces a compressive residual stress within a depth of more than 1 mm. LSP subsequently to LST has been applied in the case of bionic non-smooth 0Cr18Ni9 stainless steel surfaces fabrication and the effects of LSP and groove spacing on their wear behavior have been investigated.

The range and variety of the laser-induced microstructures on the surfaces of titanium, stainless steel, aluminum, molybdenum, and copper substrates comprise holes, bumps or spikes, bulges, undulating grooves, dimples, honeycombs, linked nanostructure-textured mound-shaped microstructures, melt-like and cauliflower-like structures. In addition, the formation of laser-induced periodic surface structures, nano-pillars, and micro-columns has also been reported. Other than that, there has been observed the formation of nano-ripples on TiO2 surface following UV femtosecond laser irradiation, the fs laser nanostructuring of nitrided alloy steels containing Cr, the LSP of plasma electrolytically oxidized aluminum 6061 alloy for improved hydrophobicity and the IR fs laser nano- and micro-texturing of a stainless steel surface combined with chemisorption of an hydrophobic agent. In general, the optimization of the laser settings toward a desired surface texture consists a tediously long procedure given the large breadth of the experimental parameters space. Laser-Based 3D Printing and Surface Texturing
fluence value, number of applied laser pulses, pulse duration, repetition rate, scanning speed, and number of scans – varying, at the same time, from metal to metal. In several applications (cutting tools, wearing parts, heat engines, medical implants, construction) for which exceptional physical and mechanical properties are required – such as high hardness, advanced thermal resistance, and chemical stability – the ceramics have established a strong foothold. LM has proven a promising tool for their texturing, especially if one takes into account the fact that conventional techniques can hardly face the issue of their machining due to the brittle and hard nature the ceramic materials exhibit. There are mainly three ceramic LM techniques: the laser-assisted chemical etching, the LM and the laser-assisted machining (LAM) one. In any case, the challenge in the laser micromachining of ceramics lies in the great scattering of common laser wavelengths from their surface restricting, thus, the localized energy absorption. According to the laser-assisted chemical etching, laser radiation excites the material surface and/or the molecules of an employed appropriate etchant acting, thus, upon the reaction between the material and the etchant. In such a way, the etching rate is mostly affected by the laser fluence value.

In LM, the absorbed high-energy density of the incident laser photons causes the breakage of the chemical bonds leading to the material ejection from the irradiated area inducing grooves formation on the ceramic surface. The mechanism underlying the material removal deals with material melting, decomposition, and evaporation. The crucial parameter for the process effectiveness employs different properties of the ceramic under treatment each time, such as, reflectivity – especially the multiple reflections in the laser-induced grooves thermal conductivity, specific heat, and latent heats of melting and evaporation. Alumina owing excellent dielectric strength, thermal stability, and conductivity has been laser textured by CO₂ laser, YAG lasers, copper vapor laser, Krf laser, and near infrared femtosecond laser. In addition, alumina has been laser machined in three dimensions (3D) by 3D laser carving; an industrial technique for ceramic manufacturing of complex shapes based on 3D CAD model slices and by the laser milling technique. In advance, it has been proposed, that, after a focused laser beam scatters two groove-cracks at two intersecting surfaces of a rectangular alumina substrate, a defocused one is applied throughout the length of the groove-cracks, generating, thus, great thermal stress leading to the two groove-cracks link together, requiring much lower energy power compared to the conventional LM technique. Several research publications report on the use of two laser beams for laser alumina texturing toward the fracture control upon the procedure. Recently, a new methodology has been mentioned for the fabrication of complex-shaped Al₂O₃ ceramic parts by combining LM and gelcasting technique. According to this technique, the unwanted ceramic powders parts are selectively removed by LM specified by a computer program, and the gelcast Al₂O₃ green bodies were machined to a designed shape by a CO₂ laser. Bearings, rocker arms, piston rings, and cams can be made by LM of silicon nitride for automotive, semiconductor, and aerospace industries purposes. CO₂ laser in air or under N₂, O₂ gas atmospheres, Nd:YAG laser and excimer laser systems have been employed in the LM of silicon nitride aiming to the micro-cracks minimization. 3D structuring of silicon nitride by employing a relatively new machining process, namely, the laser milling technique relying on CAD data has also been reported, based on an ablation operation leading to the material removal in a layer-by-layer fashion. Another broadly laser-machined ceramic is the silicon carbide. It has been treated by CO₂ laser in air or in N₂, O₂ gas atmosphere by Nd:YAG laser.
The high thermal conductivity and small thermal expansion mismatch with silicon of aluminum nitride justify its widespread use in microelectronic substrates and packages and has been laser machined with near-IR and excimer lasers. The fabrication of pH meters, fuel cells, IR radiator, pressure, and oxygen sensors employs the use of zirconia due to its unique characteristics: low thermal conductivity and friction coefficient, high fracture toughness, and good thermal shock resistance. The high thermal conductivity and small thermal expansion mismatch with silicon of aluminum nitride justify its widespread use in microelectronic substrates and packages and has been laser machined with near-IR and excimer lasers. The fabrication of pH meters, fuel cells, IR radiator, pressure, and oxygen sensors employs the use of zirconia due to its unique characteristics: low thermal conductivity and friction coefficient, high fracture toughness, and good thermal shock resistance.

Laser interference lithography (LIL) enables a scalable process for polymer substrates in the absence of any masks or templates. The produced patterns are filled. Laser interference lithography (LIL) enables a scalable process for polymer substrates in the absence of any masks or templates. The produced patterns are filled. Laser interference lithography has emerged as a technology capable to fabricate templates by irradiating an azo-polymer or a photoresist with interference patterns obtained by using two or more coherent light beams, mostly operating in continuous wave mode. In addition, the LIL-induced nano-patterning structure, following the pattern transfer, can be used in: optical devices, surface plasmon resonance sensors, metamaterials, electrodes for cross-field emission panels, large-area broadband photonic crystal membrane reflectors on glass substrates, biomaterials, micro-sieves for micro-filtration, template for self-assembly, field emission panel displays, large-area photonic crystal slabs for visible light, and micro- and nano-fluidics. The potential of the LIL technique wider employment in industry has also been mentioned.

Alternatively, the direct laser interference patterning (DLIP) technique enables a scalable process for polymer substrates structuring by direct substrate material ablation, requiring only a single processing step without solvents or heating. In DLIP, similarly to LIL, two or more coherent laser beams are brought to interference with each other on a substrate and different one- and two-dimensional periodic patterns are induced by direct ablation of the substrate – with spatial periods ranging from some hundreds nanometers up to several micrometers – in the absence of any masks or templates. The produced patterns are attributed to the periodic light intensity variation and the high light absorption by the material.
Silicon rewards a special dedication since it is an important semiconductor material with numerous applications of broad range, and has erstwhile till recently been laser surface textured for microelectronics, solar cells, or biomedical purposes. In general, micro-, submicro-, and nano-periodic patterns (e.g., grooves, pits, spikes) are induced on the Si surface depending on the laser irradiation parameters, the irradiation gas atmosphere or environment affecting the melt material distribution following ablation. In advance, near-field enhanced laser irradiation with micro-nano-sized spheres and near-field scanning optical microscope have been used. On the contrary, a non-ablative laser surface texturing technique to form a regular array of micro-bumps on Si surface by a 1090 nm continuous wave fiber laser has been proposed, besides the high transparency that Si exhibits at this wavelength. The non-ablative laser-induced micro-bumps formation was attributed to localized Si oxidation. Recently, there has been reported that upon 1064 nm picosecond laser irradiation of Si, micro-nano hierarchical pore structures are formed on its surface, which are subsequently precisely chemically etched and, finally, light-trapping structures are fabricated. LIL has also been applied for the fabrication of two-dimensional photonic crystals in silicon-on-insulator wafers and for Si texturing with thoroughly investigated wetting properties of the induced periodical nano-patterns and hierarchical structures. More recently, there has been reported the case of moth-like as well as of grating, triangle, and square surface structures induced on silicon by multi-beam LIL. Concerning the solar cells applications, sub-micrometer conical and pillar-shaped spikes have been fabricated by irradiating hydrogenated amorphous silicon thin films deposited on glass substrates with hundreds of 800 nm-wavelength, 130 fs-duration laser pulses in air and water environments, respectively. Lately, there has been reported the laser-induced formation of 300 nm period pore arrays on Si combined with electrochemical etching.

Concerning the LST of polymers, a key parameter of the procedure is the polymer molecular weight. Low molecular weight polymers with short polymer chains are volatile, whereas, the longer ones of the high molecular weight polymers melt. In this case, the material removal is due to evaporation from the polymer substrate – upon an explosive boiling procedure – in an ablation plume full of molecular fragments, ions, free electrons, neutral particles, and products from the chemical reactions between the plume components and the irradiation atmosphere. Among the laser textured polymers, poly(methyl-methacrylate) (PMMA) has received the lion’s share of the universal applied research interest, for example, for microfluidic devices fabrication, by using mainly UV laser radiation. However, from an application point of view, the thermal damage minimization of the surrounding (the laser irradiated area) material is crucial since it deteriorates both the spatial resolution and the ablation quality. Consequently, the photochemical processes which lead to the so called ‘cold’ ablation are most preferable. In general, the energy of the UV lasers photons is high enough to induce the direct bond breakage in a strongly absorbing at the irradiation wavelength organic material. It is of great importance the fact that the bulk properties of the laser textured polymers remain intact and, thus, they can be employed in bioengineering applications since the microscale topography may in fluence several properties, such as wetting properties and cell behavior. At the end, it is worth mentioning the recent laser texturing developments at the sake of tissue engineering applications, since they prove the potential spreading of the technique in this rapidly growing interdisciplinary field: the micro-channels on medical needles, the osteoblastic commitment improvement of human mesenchymal stem cells on Ti alloys, the neuronal cells cultivation on Si spikes, the fibroblasts cell culture on laser-made chitosan scaffolds and the osteoblast proliferation and morphology on metallic alloys.

6 Conclusions

This chapter has attempted to cover the laser-based 3D printing and surface texturing techniques which meet the ever increasing challenges and demands of either existing or emerging scientific fields. The superior precision and reproduction, the high working speed, the wide bandwidth of possible materials, and the exceptional degree of flexibility justify the laser fabrication techniques employment in a smorgasbord of human life domains in the industrialized countries: manufacturing, communication, military aspects, health technologies, metrology, reprography, and entertainment. The laser versatility in the ability to create structures of any desired dimension and geometry guarantees the progress of future structuring procedures. Yet, there is a long trail behind the Holy Grail of laser processing capabilities: the controllable fabrication at nanometer scale, which will provide a broad range of technical opportunities with frame and limits left to human imagination.


